Theory of the aging of precipitates by dissolution-reprecipitation (Ostwald ripening)

by

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Abstract

The theory of aging of a poorly soluble precipitate such as AgBr by dissolution-reprecipitation according to the higher solubility of small particles compared to that of large particles is developed quantitatively. Equations are given for the temporal change in the size distribution function, the average particle size and the particle number for diffusion-controlled and reaction-controlled mass transfer.

1 Problem statement

According to the GIBBS-THOMSON formula, small droplets have a higher vapor pressure or a higher solubility in a surrounding liquid phase of a second substance than large drops. In a multidisperse emulsion, matter is transported from the surface of small drops to the surface of large drops, i.e. large drops grow at the expense of small drops. Analogous processes can be found in multidisperse suspensions of crystalline substances. As an example, the grain enlargement of AgBr precipitation that occurs in the production of photographic emulsions is mentioned, which is known in the literature as OSTWALD ripening.

The task of this work is to develop the equations that describe these processes quantitatively. This assumes that agglomeration of particles does not occur or is only a side effect of minor importance. The initial state is characterized by a certain distribution function of the size of the particles. Therefore one can ask, how

1. the distribution function,

2. the average particle size and

3. the total number of particles

changes over time. The same task is handled, among others, by TODES, [15], TODES and KHRUSHCHEV, [14] as well as by LIFSHITZ and SLYOZOV, [9, 10]. The results of these authors are referred to below.

2 List of Symbols

c_0	Saturation concentration for the limit case of infinitely large particles
c_r	Saturation concentration for particles of radius r
c_r'	Concentration at the surface of particles of radius r
c	average concentration in a system of particles of different sizes
$\mathscr{D}$	Diffusion constant
$f(r,t)$	Distribution function of particle number as a function of radius r at time t according to the definition in Equation 13
$g_\mathrm{D}(t), h_\mathrm{D}(\varrho)$	Auxiliary functions for diffusion-controlled (D) and reaction-controlled (R) mass transfer, cf. Equation 53 and Equation 54
$g_\mathrm{R}(t), h_\mathrm{R}(\varrho)$	Auxiliary functions for diffusion-controlled (D) and reaction-controlled (R) mass transfer, cf. Equation 73 and Equation 74
k	Constant of the phase boundary reaction, cf. Equation 19

n	Number of moles in a single particle
$\dot{n}$	change over time in the number of moles in a single particle
r	effective particle radius, cf. Equation 3
$\dot{r}$	change in particle radius over time
$r^\star$	Radius of a particle in equilibrium with the surrounding solution
$\bar{r}_0$	mean radius in a heterodisperse dispersion at time $t = 0$
$\mathscr{R}$	Gas constant
T	Temperature
t	Time
V_m	Molar volume
Z	Total number of particles per unit volume
Z_0	Total number of particles per unit volume at time $t = 0$
$\gamma_{\mathrm{D}}, \gamma_{\mathrm{R}}$	Auxiliary parameters for diffusion-controlled (D) and reaction-controlled (R) mass transfer, cf. Equation 58 and Equation 78
$\varepsilon_0 \cdot \bar{r}_0$	Scattering of the particle size distribution at time $t = 0$
$\varepsilon \cdot \bar{r}_0$	Scattering of the particle size distribution at time t
ϱ	$\frac{r}{r^\star}$, dimensionless measure of particle size
σ	Interfacial tension
ν	stoichiometric factor
τ_D, τ_D'	Time constants of dissolution-reprecipitation for diffusion-controlled mass transfer, cf. Equation 46, Equation 60 and Equation 67
τ_R, τ_R'	Time constants of dissolution-reprecipitation for reaction-controlled mass transfer, cf. Equation 48, Equation 80 and Equation 88
φ	Volume of the disperse phase per unit volume of the dispersion

3 Thermodynamic equations

For the vapor pressure p of a droplet of radius r we have the well-known GIBBS-THOMSON equation:

$$p_r = p_0 \cdot e^{\frac{2\sigma V_m}{r\,\mathscr{R}\,T}} \,, \tag{1}$$

where p_0 is the vapor pressure for the limiting case of a flat liquid surface ($r = \infty$), σ is the surface free enthalpy, V_m is the molar volume of the condensed phase, $\mathscr{R}$ is the gas constant and T is absolute temperature. An analogous formula applies to the solubility of small droplets and small crystals in a surrounding liquid phase. In order to obtain a formula that can also be used for crystals, [2, 13], it must be assumed that the crystal which is present is in the so-called equilibrium configuration according to GIBBS-WULFF, corresponding to a minimum of the total surface energy at a given mass or number of moles of the crystal. Then the exponential function

$$\exp\left[\frac{\sigma V_m}{\mathscr{R}\,T} \cdot \frac{\partial O}{\partial V}\right]$$

arises, where σ is the mean free surface energy corresponding to the equilibrium configuration of a particle and $\frac{\partial O}{\partial V}$ is the quotient of surface change and volume change when a particle increases in size while maintaining the equilibrium configuration, the presence of which is assumed in all following considerations. In case of a spherical particle:

$$\left(V = \frac{4}{3}\pi r^3, \quad O = 4\pi r^2\right)$$

the following holds:

$$\frac{\partial O}{\partial V} = \frac{2}{r} \,, \tag{2}$$

which results in Equation 1.

Introducing the concept of the effective radius of a particle according to the definition:

$$r = 2 \cdot \frac{\partial V}{\partial O} \tag{3}$$

one can therefore write for a non-dissociating substance instead of Equation 1:

$$c_r = c_0 \cdot e^{\frac{2\sigma V_m}{r\,\mathscr{R}\,T}} \,, \tag{4}$$

where c_0 is the limit of the solubility of an infinitely large particle and c_r is the solubility of a particle with effective radius $r = 2 \cdot \left(\frac{\partial V}{\partial O}\right)$. In general, the exponent is small compared to 1 and the exponential function can therefore be developed in form of a TAYLOR series. Thus it follows:

$$c_r \cong c_0 \cdot \left[1 + \frac{2\sigma V_m}{r\,\mathscr{R}\,T}\right] \,. \tag{5}$$

This approximation fails for very small particles for which $\frac{2\sigma V_m}{r\,\mathscr{R}\,T} \gtrsim 0.3$, i.e. for particles whose radius is of the order of $3 \times 10^{-7}\,\text{cm}$ or smaller. However, the behavior of such small particles is generally practically irrelevant to the overall course of phenomena. Therefore, the approximate equation according to Equation 5 is used throughout the following.

In the case of dissociating substances (especially salts) of the general formula $A_\alpha B_\beta$, an equation corresponding to Equation 4 applies for the solubility product Lp:

$$\text{Lp}_r = \text{Lp}_0 \cdot e^{\frac{2\sigma V_m}{r\,\mathscr{R}\,T}} \ . \tag{6}$$

In the case of complete dissociation and the presence of equivalent amounts of A and B in the solution, one can calculate the gross solubility c (moles of $A_\alpha B_\beta$ per unit volume) by the individual concentrations c_A and c_B of A and B respectively as follows:

$$c = \frac{c_A}{\alpha} = \frac{c_B}{\beta} \ . \tag{7}$$

Using the defining equation of the solubility product

$$\text{Lp} = c_A^\alpha \cdot c_B^\beta \tag{8}$$

it follows from Equation 6 and Equation 7 at total dissociation

$$c_r^{\alpha+\beta} = c_0^{\alpha+\beta} \cdot e^{\frac{2\sigma V_m}{r\,\mathscr{R}\,T}} \ . \tag{9}$$

Using the series expansion for the exponential function we get from Equation 9:

$$c_r = c_0 \cdot \left[1 + \frac{2\sigma V_m}{(\alpha+\beta) \cdot r\,\mathscr{R}\,T} \right] \ , \quad \text{if} \ \ \frac{c_A}{\alpha} = \frac{c_B}{\beta} \ . \tag{10}$$

In many cases, component A or B is present in a relatively large excess in the solution. If there is an excess of B, c_B is given as a practically constant value. Then one usually defines solubility as the total concentration of the minority component A in the solution at equilibrium and obtains from Equation 6 and Equation 8 by series expansion of the exponential function:

$$c_r = c_0 \cdot \left[1 + \frac{2\sigma V_m}{\alpha r\,\mathscr{R}\,T} \right] \ . \tag{11}$$

An analogous formula for the solubility with β instead of α is obtained in the case of an excess of A measured as equilibrium concentration of B.

In general one can write:

$$c_r = c_0 \cdot \left[1 + \frac{2\sigma V_m}{\nu r\,\mathscr{R}\,T} \right] \ . \tag{12}$$

In Equation 12 $\nu = 1$ for undissociated substances. Even with dissociating substances, $\nu = 1$ if there is an excess of B and the formula $AB_{\beta/\alpha}$ or if there is an excess of A and the formula $A_{\alpha/\beta}B$ is used as a basis for calculating the molar volume V_m. The above notation of the formula is assumed in the following, as this is also the easiest way to formulate the diffusion and reaction equations. Only in the case of equivalence of A and B in the solution should $\nu = \alpha + \beta$ be set based on the formula $A_\alpha B_\beta$ to calculate the molar volume V_m.

4 General equations for the time change of the distribution function in a polydisperse system

To describe a multidisperse system of particles distributed in a second phase, the distribution function $f(r, t)$ is introduced, the defining equation of which is:

$$f(r, t) = \lim_{\Delta r = 0} \frac{\mathcal{N}(r, r + \Delta r, t)}{\Delta r},$$

(13)

where $\mathcal{N}(r, r + \Delta r, t)$ is the number of particles per unit volume of the disperse system with radii between r and $r + \Delta r$ at time t.

The number of particles per unit of volume that reach and exceed a certain radius through growth per unit of time is equal to the product of the distribution function and the change in radius of the individual particle over time, i.e. equal to $f \cdot \frac{\mathrm{d}r}{\mathrm{d}t}$. The change in the distribution function over time for a given value r then results as the negative value of the divergence[1] of $f \cdot \frac{\mathrm{d}r}{\mathrm{d}t}$. This results in the differential equation already given by LIALIKOV, PISCOUNOVA, CHIPILOV and CERDYCEV, [8]:

$$\frac{\partial f}{\partial t} = -\frac{\partial(f\dot{r})}{\partial r}.$$

(14)

For the total number Z of particles per unit volume of a dispersion it follows from Equation 13:

$$Z = \int_0^\infty f(r, t)\,\mathrm{d}r.$$

(15)

The time decrease in Z is given by the number of particles that approach the radius $r = 0$ per unit volume of the dispersion and per unit time, i.e. by the limit of $-f \cdot \dot{r}$ for $r = 0$. Thus it follows:

$$-\frac{\mathrm{d}Z}{\mathrm{d}t} = -\frac{\mathrm{d}}{\mathrm{d}t}\left(\int_0^\infty f(r, t)\,\mathrm{d}r\right) = -\lim_{r=0}(f \cdot \dot{r}).$$

(16)

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[1]The divergence is an operator, which takes in the vector-valued function, i.e. the distribution function over time defining this vector field, and outputs a scalar-valued function $\frac{\mathrm{d}r}{\mathrm{d}t}$ measuring the change in radius of the particle at each point.

An evaluation of Equation 14 and Equation 16 requires knowledge of the change in particle radius r over time. The corresponding equations can be found in section 5. Another important general equation is obtained by calculating the fraction φ of the disperse phase, i.e. the volume of the dispersed particles per unit volume of the dispersion. Using the distribution function this yields:

$$\varphi = \int_0^\infty \frac{4\pi r^3}{3} \cdot f(r,t)\,\mathrm{d}r\,. \tag{17}$$

The temporal change in the dissolved fraction corresponding to the temporal increase in the mean particle radius is generally negligible. As long as the dispersed substance is neither formed nor consumed by chemical reaction, φ is time-independent and so is the integral on the right-hand side of Equation 17. This relationship will be used several times below.

5 General equations for diffusion-controlled and reaction-controlled mass transfer

The time change $\dot{n}$ in the number of moles of a spherical particle of radius r of a non-dissociated substance is equal to the negative value of the product of the diffusion coefficient $\mathscr{D}$, surface area $4\pi r^2$ and the concentration gradient on the surface. If the concentration in the environment is significantly smaller than the concentration within the particle, then the concentration gradient for quasi-stationary conditions is $\frac{c'_r - c}{r}$, where c'_r is the concentration at the particle surface and c means the average concentration of the solution, [11, 16]. So one obtains:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \dot{n} = -4\pi r\,\mathscr{D}\cdot(c'_r - c)\,. \tag{18}$$

This assumes that the distance between the next neighboring particles is large compared to their radius. With regard to Equation 17, this requirement is equivalent to the condition $\varphi \ll 1$ corresponding to a sufficiently small volume fraction of the dispersed phase.

The above equation also applies to dissociated salts $A_\alpha B_\beta$ if, in the case of equivalence, the solubility is defined according to Equation 7. Furthermore, Equation 18 also applies to an excess of B, if the calculation of the number of moles is based on the formula $AB_{\beta/\alpha}$ and with c there is understood the concentration of A in the solution and $\mathscr{D}$ means the diffusion coefficient of A. If there is an excess of A, the formula $A_{\alpha/\beta}B$ should be used.

The mass transfer at an interface between a uniform liquid phase and the gas phase or between two liquid phases without the presence of additional surface-active substances is generally hardly inhibited, so that local equilibrium at the phase boundary can be expected. As a limiting case for the latter one can set that $c'_r = c_r$,

where c_r is given by Equation 12.

The transfer of ions from a crystal into the surrounding solution and also the reverse process of the transfer of ions from a solution into a crystal can also be practically uninhibited, e.g. in the case of AgCl or $KClO_4$, [4, 3]. In other cases, e.g. $BaSO_4$, noticeable deviations from equilibrium can be observed, since the hydration or dehydration of higher-value ions in particular can have a significant activation energy, [4]. In order to describe the processes also in such systems, it is assumed that the rate of mass transfer at the phase boundary per unit area is equal to the product of a rate constant and the difference between the equilibrium concentration c_r and the concentration c_r' at the surface. For the change in the number of moles of a particle with surface area $4\pi r^2$ one gets:

$$\dot{n} = -4\pi r^2 k \cdot (c_r - c_r') \,, \tag{19}$$

where k means the rate constant of mass transfer.

The relationships for nearly spherical, e.g. cube-shaped crystals are analogous. However, if the effective particle radius introduced in Equation 3 is used, additional numerical factors of the order of magnitude 1 appear in Equation 18 and Equation 19. This will be ignored below. The results of the following calculations therefore only have semi-quantitative significance for non-spherical particles. The special approaches for the growth of long needles or thin plates, [16], can be ignored here, since according to section 3 crystals are assumed to be in the equilibrium configuration.

By equating the right-hand sides of Equation 18 and Equation 19 one obtains an equation for calculating c_r'. By solving for c_r' we get:

$$c_r' = \frac{krc_r + \mathscr{D}\,c}{kr + \mathscr{D}} \,. \tag{20}$$

Introducing Equation 20 in Equation 18 or Equation 19 yields:

$$\dot{n} = -\frac{4\pi r^2 k \, \mathscr{D}}{kr + \mathscr{D}} \cdot (c_r - c) \,. \tag{21}$$

For the time change in the volume $\frac{4\pi}{3}r^3$ of a single particle we get:

$$\frac{\mathrm{d}}{\mathrm{d}t}\left(\frac{4\pi r^3}{3}\right) = 4\pi r^2 \cdot \dot{r} = \dot{n} \cdot V_m \,, \tag{22}$$

where V_m means the molar volume of the dispersed substance.

From Equation 21 and Equation 22 it follows that:

$$\dot{r} = \frac{\dot{n}V_m}{4\pi r^2} = -\frac{k\,\mathscr{D}\,V_m}{kr + \mathscr{D}} \cdot (c_r - c) \,. \tag{23}$$

The following limiting cases are to be noted:

1. If $kr \gg \mathscr{D}$, then $c_r' \cong c_r$ corresponds to practical reach of equilibrium on the drop surface, i.e. the mass transfer is controlled by diffusion. It therefore follows from Equation 23:

$$\dot{r} = -\frac{\mathscr{D} V_m}{r} \cdot (c_r - c), \quad \text{if } kr \gg \mathscr{D} . \tag{24}$$

2. Conversely, if $kr \ll \mathscr{D}$, then $c_r' \cong c$ corresponds to the practically reached diffusion equilibrium between the surface and the interior of the dispersing liquid, i.e. the mass transfer is reaction-controlled. It therefore follows from Equation 23:

$$\dot{r} = -kV_m \cdot (c_r - c), \quad \text{if } kr \ll \mathscr{D} . \tag{25}$$

The change in the concentration of solute over time is equal to the negative value of the sum of the changes in the number of moles over time of the individual particles per unit volume of the dispersion:

$$\frac{\partial c}{\partial t} = -\int_0^\infty \dot{n}(r) \cdot f(r, t)\, \mathrm{d}r . \tag{26}$$

If the amount of substance contained in the dispersed droplets or crystals is significantly larger than the amount of substance dissolved in the dispersing liquid, it can be assumed that the amount of substance that goes into solution from the small particles per unit of time is practically equal to the amount of substance deposited on the large particles and in comparison to this, under quasi-stationary conditions, the change in the amount of substance $\frac{\partial c}{\partial t}$ in the solution corresponding to an increase in the average particle radius is vanishingly small. Substituting Equation 12 and Equation 21 into Equation 26 for $\frac{\partial c}{\partial t} = 0$ gives a conditional equation for the concentration c inside the dispersing liquid with the result:

$$\frac{c}{c_0} = 1 + \frac{2\sigma V_m}{\nu \mathscr{R} T} \cdot \frac{\int_0^\infty f(r,t) \cdot \frac{r\,\mathrm{d}r}{kr+\mathscr{D}}}{\int_0^\infty f(r,t) \cdot \frac{r^2\,\mathrm{d}r}{kr+\mathscr{D}}} . \tag{27}$$

Inserting Equation 12 and Equation 27 into Equation 23 gives:

$$\dot{r} = -\frac{2\sigma c_0 V_m^2}{\nu r \mathscr{R} T} \frac{k\mathscr{D}}{kr + \mathscr{D}} \cdot \left[1 - \frac{r \cdot \int_0^\infty f(r,t) \cdot \frac{r\,\mathrm{d}r}{kr+\mathscr{D}}}{\int_0^\infty f(r,t) \cdot \frac{r^2\,\mathrm{d}r}{kr+\mathscr{D}}} \right] . \tag{28}$$

From Equation 28 one obtains for the radius $r^\star$ of a particle that is in equilibrium with the ambient concentration and for which accordingly $\dot{r} = 0$:

$$r^\star = \frac{\int_0^\infty f(r,t) \cdot \frac{r^2\,\mathrm{d}r}{kr+\mathscr{D}}}{\int_0^\infty f(r,t) \cdot \frac{r\,\mathrm{d}r}{kr+\mathscr{D}}} . \tag{29}$$

Using Equation 29 one can write Equation 28 in the simplified form

$$\dot{r} = \frac{2\sigma c_0 V_m^2}{\nu r \, \mathscr{R} \, T} \frac{k \, \mathscr{D}}{kr + \mathscr{D}} \cdot \left(\frac{r}{r^\star} - 1 \right) \,. \tag{30}$$

Inserting Equation 30 in Equation 14 gives:

$$\frac{\partial f(r,t)}{\partial t} = -\frac{2\sigma c_0 V_m^2}{\nu r^\star \, \mathscr{R} \, T} \cdot \frac{\partial}{\partial r} \left[\frac{k \, \mathscr{D}}{kr + \mathscr{D}} \cdot (r - r^\star) \cdot \frac{f(r,t)}{r} \right] \,. \tag{31}$$

The following limiting cases are to be noted:

1. If $k\bar{r} \gg \mathscr{D}$ (with $\bar{r}$ as the mean droplet radius), then for the majority of the droplets one has diffusion-controlled mass transfer. In this case Equation 29 and Equation 31 are simplified. $r^\star$ becomes equal to the mean radius $\bar{r}$:

$$r^\star = \frac{\int_0^\infty f(r,t) \cdot r \, \mathrm{d}r}{\int_0^\infty f(r,t) \, \mathrm{d}r} = \bar{r} \,. \tag{32}$$

For $k\bar{r} \gg \mathscr{D}$ it further follows from Equation 31:

$$\frac{\partial f(r,t)}{\partial t} = -\frac{2\sigma \, \mathscr{D} \, c_0 V_m^2}{\nu r^\star \, \mathscr{R} \, T} \cdot \frac{\partial}{\partial r} \left[\frac{(r - r^\star) \cdot f(r,t)}{r^2} \right] \,. \tag{33}$$

2. If $k\bar{r} \ll \mathscr{D}$, then for the majority of droplets one has reaction-controlled mass transfer. For this, Equation 29 and Equation 31 simplify to:

$$r^\star = \frac{\int_0^\infty f(r,t) \cdot r^2 \, \mathrm{d}r}{\int_0^\infty f(r,t) \cdot r \, \mathrm{d}r} \,, \tag{34}$$

$$\frac{\partial f(r,t)}{\partial t} = -\frac{2\sigma k c_0 V_m^2}{\nu r^\star \, \mathscr{R} \, T} \cdot \frac{\partial}{\partial r} \left[\frac{(r - r^\star) \cdot f(r,t)}{r} \right] \,. \tag{35}$$

6 Equations for systems in which the initial distribution function is given by a narrow Gaussian curve

With the help of Equation 31 one can basically calculate the distribution function f for any time $t > 0$ if the initial distribution $f(r, t = 0)$ is given. For any given initial distribution one has to use numerical methods, e.g. RUNGE-KUTTA or ADAMS-STÖRMER. Furthermore, one can ask for an analytical solution provided that the initial distribution is given by an analytical function. As a special case,

assume that $f(r, t = 0)$ is given by a narrow GAUSSian curve:

$$f(r, t = 0) = C_0 \cdot e^{-\frac{1}{2} \cdot \left(\frac{r - \bar{r}_0}{\varepsilon_0 \bar{r}_0}\right)^2} . \tag{36}$$

In Equation 36 C_0 is a constant, $\bar{r}_0$ is the mean particle radius at time $t = 0$ and $\varepsilon_0 \bar{r}_0$ is the scatter of the initial distribution, where ε_0 must be $\ll 1$ so that the GAUSSian curve is narrow.

If one integrates the distribution function from $r = 0$ to $r = \infty$, one gets according to Equation 15 the initially existing total number Z_0 of particles per unit volume of the dispersion. With

$$u = \frac{r - \bar{r}_0}{\sqrt{2} \cdot \varepsilon_0 \bar{r}_0}$$

as an integration variable one gets for $\varepsilon_0 \ll 1$:

$$\int_0^\infty f(r, t = 0)\, \mathrm{d}r = \sqrt{2}\varepsilon_0 \bar{r}_0 C_0 \cdot \int_{-\frac{1}{\sqrt{2}\varepsilon_0}}^\infty e^{-u^2}\, \mathrm{d}u$$

$$\cong \sqrt{2}\varepsilon_0 \bar{r}_0 C_0 \cdot \int_{-\infty}^{+\infty} e^{-u^2}\, \mathrm{d}u = \sqrt{2\pi}\varepsilon_0 \bar{r}_0 C_0 = Z_0 . \tag{37}$$

This gives the value for the constant C_0 in Equation 36:

$$C_0 = \frac{Z_0}{\sqrt{2\pi} \cdot \varepsilon_0 \bar{r}_0} . \tag{38}$$

We then examine how the distribution function $f(r, t)$ changes for $t > 0$. Initially, only the behavior within sufficiently short times is considered, during which the distribution function gradually broadens, but still remains relatively narrow (cf. Figure 1). Then one can assume that $f(r, t)$ also for $t > 0$ is represented by a Gaussian curve and can be approximated with the spread $\varepsilon(t)\bar{r}_0 > \varepsilon_0 \bar{r}_0$, where $\varepsilon(t) \ll 1$. Accordingly it is set:

$$f(r, t) = C(t) \cdot e^{-\frac{1}{2} \cdot \left(\frac{r - \bar{r}_0}{\varepsilon(t)\bar{r}_0}\right)^2} . \tag{39}$$

Since for $\varepsilon(t) \ll 1$ the proportion of particles with molecular dimensions is vanishingly small, initially no particles disappear through complete dissolution. Therefore, the number of particles per unit volume remains the same Z_0. With an equation analogous to Equation 37 we get:

$$C(t) = \frac{Z_0}{\sqrt{2\pi} \cdot \varepsilon(t)\bar{r}_0} . \tag{40}$$
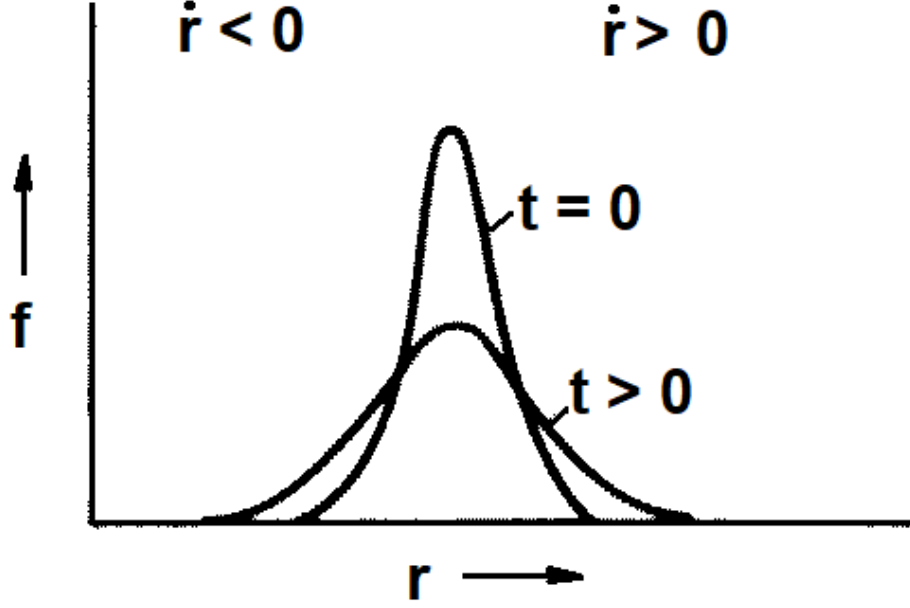
Figure 1: Distribution function after a given time t, provided that the distribution function for $t = 0$ is given by a narrow GAUSSian curve

From Equation 39 and Equation 40 it follows:

$$f(r,t) = \frac{Z_0}{\sqrt{2\pi} \cdot \varepsilon(t)\bar{r}_0} \cdot e^{-\frac{1}{2}\cdot\left(\frac{r-\bar{r}_0}{\varepsilon(t)\bar{r}_0}\right)^2} . \tag{41}$$

In the case of a narrow GAUSS curve one can set $r^\star = \bar{r}_0$ in Equation 31, and also $r \cong \bar{r}_0$, insofar as r appears as a factor. This gives us a simplified form of Equation 31:

$$\frac{\partial f(r,t)}{\partial t} = -\frac{2\sigma c_0 V_m^2}{\nu \bar{r}_0^2 \, \mathscr{R} \, T} \frac{k\,\mathscr{D}}{k\bar{r}_0 + \mathscr{D}} \cdot \frac{\partial}{\partial r}\left[(r - \bar{r}_0) \cdot f(r,t)\right] . \tag{42}$$

Substituting Equation 41 into Equation 42 gives the differential equation for $\varepsilon(t)$:

$$\frac{\mathrm{d}\varepsilon(t)}{\mathrm{d}t} = \frac{2\sigma c_0 V_m^2}{\nu \bar{r}_0^2 \, \mathscr{R} \, T} \frac{k\,\mathscr{D}}{k\bar{r}_0 + \mathscr{D}} \cdot \varepsilon(t) . \tag{43}$$

Since r no longer appears in Equation 43, the heuristic approach in Equation 39 is justified.
Taking into account the initial condition $\varepsilon(t = 0) = \varepsilon_0$, integrating Equation 43 results in:

$$\varepsilon(t) = \varepsilon_0 \cdot e^{\frac{t}{\tau}} \tag{44}$$

wherein for abbreviation τ was set to

$$\tau = \frac{\nu \bar{r}_0^2 \, \mathscr{R} \, T}{2\sigma c_0 V_m^2} \frac{k \bar{r}_0 + \mathscr{D}}{k \, \mathscr{D}} \ . \tag{45}$$

The following limiting cases are to be noted:

1. If $k\bar{r}_0 \gg \mathscr{D}$, i.e. for diffusion-controlled mass transfer it follows:

$$\tau_{\mathrm{D}} = \frac{\nu \bar{r}_0^3 \, \mathscr{R} \, T}{2\sigma \, \mathscr{D} \, c_0 V_m^2} \ . \tag{46}$$

According to Equation 46, the time constant τ_{D} for diffusion-controlled mass transfer is proportional to the third power of the average particle radius $\bar{r}_0$, and therefore grows disproportionately quickly with increasing average particle radius. A double mean radius corresponds to eight times the value of the time constant. Basically, the speed of dissolution-reprecipitation is always finite. In practice, however, the dissolution-reprecipitation is only noticeable when the time constant τ_{D} is of the order of magnitude of the observation time t_{obs} or smaller. If τ_{D} is larger than t_{obs}, then the size distribution can be considered practically stable for most purposes. Thus, from Equation 46 one obtains as a condition for practical stability of a size distribution:

$$\bar{r}_0 \gtrsim \sqrt[3]{\frac{2\sigma \, \mathscr{D} \, c_0 V_m^2 \cdot t_{\mathrm{obs}}}{\nu \, \mathscr{R} \, T}} \ . \tag{47}$$

2. If $k\bar{r}_0 \ll \mathscr{D}$, i.e. for reaction-controlled mass transfer, it follows:

$$\boxed{\tau_{\mathrm{R}} = \frac{\nu \bar{r}_0^2 \, \mathscr{R} \, T}{2\sigma k c_0 V_m^2}} \ . \tag{48}$$

According to Equation 48 τ_{R} is only proportional to the square of the mean droplet radius. In view of the weaker dependence for τ_{R} as a function of $\bar{r}_0$ compared to the corresponding dependence for τ_{D} according to Equation 46, a formula analogous to Equation 47 can be written down with only a lower degree of approximation. Despite this limitation, the condition for the practical stability of a size distribution for a given observation time is given analogously to Equation 47:

$$\boxed{\bar{r}_0 \gtrsim \sqrt{\frac{2\sigma k c_0 V_m^2 \cdot t_{\mathrm{obs}}}{\nu \, \mathscr{R} \, T}}} \ . \tag{49}$$

7 The behavior of a polydisperse system over long periods of time with diffusion-controlled mass transfer

If the distribution function is initially given by a narrow GAUSS curve, the distribution curve will be broader with increasing time and the distribution function also assumes finite values for $r \cong 0$, so that particles according to Equation 16 disappear.

From Equation 30 one obtains for the time change in the radius of a single particle for diffusion-controlled mass transfer $(kr \gg \mathscr{D})$ for $r \ll r^{\star}$:

$$-\dot{r} = \frac{2\sigma \, \mathscr{D} \, c_0 V_m^2}{\nu r^2 \, \mathscr{R} \, T} \, . \tag{50}$$

Inserting Equation 50 in Equation 16 yields:

$$-\frac{\mathrm{d}Z}{\mathrm{d}t} = \lim_{r=0} \left[\frac{2\sigma \, \mathscr{D} \, c_0 V_m^2 \cdot f(r,t)}{\nu r^2 \, \mathscr{R} \, T} \right] \, . \tag{51}$$

Since the right hand side of Equation 51 has a certain finite value under the conditions mentioned, it follows that $f(r,t)$ increases proportionally to r^2 for $r \cong 0$. It is tentatively assumed that for longer observation times the distribution function $f(r,t)$ can be represented as the product of a pure time function $g_{\mathrm{D}}(t)$ and a function of the radius ratio

$$\varrho = \frac{r}{r^{\star}(t)} \tag{52}$$

where $r^{\star}$ is in turn a function of time. Taking into account the proportionality of f with r^2 for small values of r, let:

$$f(r,t) = g_{\mathrm{D}} \varrho^2 h_{\mathrm{D}}(\varrho) \, , \tag{53}$$

where as normalization

$$h_{\mathrm{D}}(\varrho = 0) = 1 \tag{54}$$

should apply.

With regard to Equation 32 and Equation 53, the function $h_{\mathrm{D}}(\varrho)$ must satisfy the condition

$$\int_0^{\infty} h_{\mathrm{D}}(\varrho) \cdot \varrho^2 \, \mathrm{d}\varrho = \int_0^{\infty} h_{\mathrm{D}}(\varrho) \cdot \varrho^3 \, \mathrm{d}\varrho \, . \tag{55}$$

Substituting Equation 53 into Equation 17 gives by observing Equation 52:

$$g_{\mathrm{D}}(t) = \frac{3\varphi}{4\pi \left[r^{\star}(t) \right]^4 \cdot \int_0^{\infty} h_{\mathrm{D}}(\varrho) \varrho^5 \, \mathrm{d}\varrho} \, . \tag{56}$$

By inserting Equation 50, Equation 52 and Equation 53 into Equation 16 and eliminating $g_D(t)$ with the help of Equation 56, it follows:

$$\frac{\mathrm{d}r^\star}{\mathrm{d}t} = \frac{2\sigma\,\mathscr{D}\,c_0 V_m^2}{3\nu\gamma_D\,[r^\star(t)]^2\,\mathscr{R}\,T}\,,\tag{57}$$

where for abbreviation:

$$\gamma_D = \int_0^\infty h_D(\varrho)\varrho^2\,\mathrm{d}\varrho\,.\tag{58}$$

If the size distribution as a function of r is already given at time $t = 0$ by the general form according to Equation 53, then by integrating Equation 57 it follows that:

$$r^\star(t) = r^\star(t = 0)\cdot\sqrt[3]{1 + \frac{t}{\tau_D'}}\,,\tag{59}$$

where τ_D' is a constant with the dimension of a time:

$$\tau_D' = \frac{\nu\gamma_D\,[r^\star(t = 0)]^3\,\mathscr{R}\,T}{2\sigma\,\mathscr{D}\,c_0 V_m^2}\,.\tag{60}$$

Using Equation 56 and Equation 59 one gets from Equation 53:

$$f(r,t) = \frac{\varrho^2\cdot h_D(\varrho)}{\left(1 + \frac{t}{\tau_D'}\right)^{\frac{4}{3}}}\cdot\text{const.}\tag{61}$$

Inserting Equation 61 into Equation 33 gives, taking into account Equation 52, Equation 59 and Equation 60 the differential equation:

$$\left(\frac{\varrho^3}{\gamma_D} - 3\varrho + 3\right)\cdot\frac{\mathrm{d}h_D(\varrho)}{\mathrm{d}\varrho} + \left(\frac{6\varrho^2}{\gamma_D} - 3\right)\cdot h_D(\varrho) = 0\,.\tag{62}$$

Since the time t no longer appears explicitly in Equation 62, the tentative approach in Equation 53 is justified for quasi-stationary conditions. To calculate the function $h_D(\varrho)$ from Equation 62, it is necessary to know the parameter γ_D, whose value is determined by Equation 55.

If one multiplies Equation 62 by ϱ^3 and performs integration by parts between $\varrho = 0$ and ϱ, one gets:

$$\left[\left(\frac{\varrho^3}{\gamma_D} - 3\varrho + 3\right)\cdot\varrho^3 h_D(\varrho)\right] + 9\cdot\left[\int_0^\varrho h_D(\varrho)\cdot\varrho^3\,\mathrm{d}\varrho - \int_0^\varrho h_D(\varrho)\cdot\varrho^2\,\mathrm{d}\varrho\right] = 0\,.\tag{63}$$

In Equation 63 the difference of the integrals for $\varrho \to \infty$ vanishes with respect to Equation 55. This results in the equivalent condition for determining the parameter

γ_D instead of Equation 55:

$$\lim_{\varrho=\infty}\left[\left(\frac{\varrho^3}{\gamma_D}-3\varrho+3\right)\cdot\varrho^3 h_D(\varrho)\right]=0\,.\tag{64}$$

The expression

$$\frac{\varrho^3}{\gamma_D}-3\varrho+3$$

appearing in Equation 62 to Equation 64 has a minimum for $\varrho=\sqrt{\gamma_D}$ with an associated function value $3-2\cdot\sqrt{\gamma_D}$. If one heuristically sets the latter expression equal to zero, one gets $\gamma_D=9/4$ and hereby from Equation 62:

$$\frac{\mathrm{d}\ln(h_D)}{\mathrm{d}\varrho}=-\frac{\frac{24}{9}\varrho^2-3}{\frac{4}{9}\varrho^3-3\varrho+3}=-\frac{\frac{7}{3}}{3+\varrho}-\frac{\frac{11}{3}\varrho-4}{\left(\frac{3}{2}-\varrho\right)^2}\,.\tag{65}$$

Integrating and taking into account Equation 54 gives:

$$h_D\left(\varrho\leqq\frac{3}{2}\right)=\left(\frac{3}{3+\varrho}\right)^{\frac{7}{3}}\cdot\left(\frac{\frac{3}{2}}{\frac{3}{2}-\varrho}\right)^{\frac{11}{3}}\cdot e^{-\frac{\varrho}{\frac{3}{2}-\varrho}}\,.\tag{66a}$$

$$h_D\left(\varrho\geqq\frac{3}{2}\right)=0\,.\tag{66b}$$

With Equation 66a and Equation 66b we have Equation 64 for both $\varrho=\infty$ and for the practical upper limit $\varrho=3/2$ fulfilled. If, on the other hand, one assumes $\gamma_D<9/4$ or $\gamma_D>9/4$, then Equation 64 cannot be fulfilled. For $\gamma_D<9/4$, the function $h_D(\varrho)$ calculated from Equation 62 becomes inversely proportional to ϱ^6 for large values of ϱ and the left side of Equation 64 tends to a finite limit. For $\gamma_D>9/4$, $h_D(\varrho)$ approaches infinity at a finite value of ϱ and Equation 64 can also not be fulfilled. Thus, $\gamma_D=9/4$ is the only value for γ_D that satisfies Equation 64. With $\gamma_D=9/4$ one gets from Equation 60:

$$\tau_D'=\frac{9\nu\left[r^\star(t=0)\right]^3\mathscr{R}\,T}{8\sigma\,\mathscr{D}\,c_0 V_m^2}\,.\tag{67}$$

Inserting Equation 66a into Equation 61 yields:

$$f(r,t) = \frac{\text{const.}}{\left(1 + \frac{t}{\tau_D'}\right)^{\frac{4}{3}}} \cdot \varrho^2 \cdot \left(\frac{3}{3+\varrho}\right)^{\frac{7}{3}} \cdot \left(\frac{\frac{3}{2}}{\frac{3}{2} - \varrho}\right)^{\frac{11}{3}} \cdot e^{-\frac{\varrho}{\frac{3}{2} - \varrho}}$$

$$\text{for} \quad \varrho = \frac{r}{r^\star(t)} \leqq \frac{3}{2}, \tag{68a}$$

$$f(r,t) = 0 \quad \text{for} \quad \varrho = \frac{r}{r^\star(t)} \geqq \frac{3}{2}, \tag{68b}$$

where $r^\star(t)$ is given by Equation 59. Equation 68a and Equation 68b are identical to the result of a calculation by LIFSHITZ and SLYOZOV, [9, 10], but their derivation however does not appear to be completely satisfactory, since there is no corresponding relationship like Equation 55 as a basis for determining the parameter γ_D. For a discussion of further details of Equation 68a and Equation 68b one may refer to the works of LIFSHITZ and SLYOZOV, [9, 10].

From Equation 68a one obtains for the value of ϱ, at which f or $\ln(f)$ has a maximum as a function of ϱ, the equation $16\varrho^3 + 27\varrho - 54 = 0$ with the solution $\varrho = 1.135$.
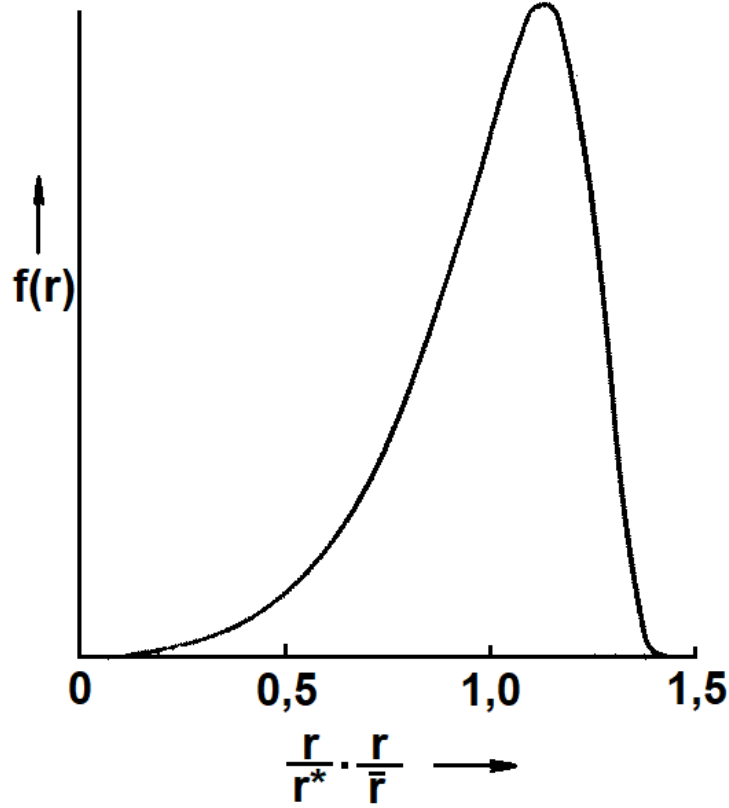

Figure 2: Quasi-stationary distribution curve for diffusion-controlled mass transfer

Figure 2 shows the course of the distribution function obtained in this way for diffusion-controlled mass transfer.

For $t \gg \tau'_{\mathrm{D}}$ one obtains from Equation 59 and Equation 67 with $\bar{r} = r^{\star}$ according to Equation 64 the approximate equation:

$$\bar{r}(t) \cong \bar{r}(t=0) \cdot \sqrt[3]{\frac{t}{\tau'_{\mathrm{D}}}} = \sqrt[3]{\frac{8\sigma \, \mathscr{D} \, c_0 V_m^2 \cdot t}{9\nu \, \mathscr{R} \, T}},$$

(69)

if $k\bar{r} \gg \mathscr{D}$ and $t \gg \tau'_{\mathrm{D}}$ or $\bar{r}(t) \gg \bar{r}(t=0)$.

Equation 59 assumes that the quasi-stationary distribution according to Equation 53 and Equation 66a as well as Equation 66b already existed for $t = 0$. However, if the distribution function for $t = 0$ is given by a moderately broad GAUSS curve, then the initial distribution transforms, according to the formulas of section 6, within a few time intervals $\tau_{\mathrm{D}} = \frac{4}{9} \cdot \tau'_{\mathrm{D}}$ into the quasi-stationary distribution existing for longer test times, so that Equation 69 can also be used in this case.

Furthermore, the particle number Z per unit volume of the dispersion can be calculated as a function of time. If according to Equation 53 the distribution function for $t \geqq 0$ is the product of a function of time and a function of $\varrho = r/r^{\star} = r/\bar{r}$, then the average particle volume is proportional to $\bar{r}^3$. Since the time-independent volume fraction φ of the dispersed particles is equal to the product of Z and the average particle volume, Z is inversely proportional to $\bar{r}^3$. So using Equation 59 it follows:

$$Z(t) = \frac{Z(t=0)}{1 + \frac{t}{\tau'_{\mathrm{D}}}}, \qquad \text{if } \; k\bar{r} \gg \mathscr{D} \; .$$

(70)

It is noteworthy that the process of dissolution-reprecipitation assumed above as the cause of the decrease in the number of particles results in the same formal time law that SMOLUCHOWSKI, [11, 12], obtained for the reduction of the number of particles by aggregation of colliding particles in the so-called rapid coagulation. In the formula of SMOLUCHOWSKI, which corresponds to the time law of a second-order reaction, the time constant is inversely proportional to $Z(t=0)$, while the constant τ'_{D} in Equation 70 according to Equation 67 is proportional to $[r^{\star}(t=0)]^3$ but independent of $Z(t=0)$.

Relationships analogous to Equation 69 and Equation 70 can already be found in the work of TODES, [15], but without calculating the quasi-stationary distribution function in Equation 68a and Equation 68b.

8 The behavior of a polydisperse system over long periods of time with reaction-controlled mass transfer

For reaction-controlled mass transfer, the calculation must be carried out in the same way as in section 7.

From Equation 30 for the time change of a single particle one obtains for reaction-controlled mass transfer ($kr \ll \mathscr{D}$) for $r \ll r^{\star}$:

$$-\frac{\mathrm{d}r}{\mathrm{d}t} = -\dot{r} = \frac{2\sigma k c_0 V_m^2}{\nu r \,\mathscr{R}\, T}\,. \tag{71}$$

Insertion of Equation 71 into Equation 16 yields:

$$-\frac{\mathrm{d}Z}{\mathrm{d}t} = \lim_{r=0}\left[\frac{2\sigma k c_0 V_m^2 f(r,t)}{\nu r \,\mathscr{R}\, T}\right]\,. \tag{72}$$

Since the right-hand side of Equation 72 is finite under the conditions assumed here, it follows that $f(r,t)$ for $r \cong 0$ increases proportionally with r or ϱ. Analogous to Equation 53, but here with the factor ϱ instead of ϱ^2, let:

$$f(r,t) = g_{\mathrm{R}}(t)\varrho h_{\mathrm{R}}(\varrho)\,, \tag{73}$$

where again $\varrho = \frac{r}{r^{\star}(t)}$ according to Equation 52 and in the sense of normalization

$$h_{\mathrm{R}}(\varrho = 0) = 1\,. \tag{74}$$

With regard to Equation 34, the function $h_{\mathrm{R}}(\varrho)$ must satisfy the condition

$$\int_0^{\infty} h_{\mathrm{R}}(\varrho) \cdot \varrho^2 \,\mathrm{d}\varrho = \int_0^{\infty} h_{\mathrm{R}}(\varrho) \cdot \varrho^3 \,\mathrm{d}\varrho\,. \tag{75}$$

Inserting Equation 73 into Equation 17 gives, taking Equation 52 into account:

$$g_{\mathrm{R}}(t) = \frac{3\varphi}{4\pi\left[r^{\star}(t)\right]^4 \cdot \int_0^{\infty} h_{\mathrm{R}}(\varrho) \cdot \varrho^4 \,\mathrm{d}\varrho}\,. \tag{76}$$

By substituting Equation 71 and Equation 72 into Equation 16 using Equation 52 and eliminating $g_{\mathrm{R}}(t)$ with the help of Equation 76 it follows:

$$\frac{\mathrm{d}r^{\star}}{\mathrm{d}t} = \frac{2\sigma k c_0 V_m^2}{3\nu\gamma_{\mathrm{R}}\left[r^{\star}(t)\right]\mathscr{R}\, T} \tag{77}$$

with

$$\gamma_R = \int_0^\infty h_R(\varrho) \cdot \varrho \, d\varrho \,. \tag{78}$$

If the size distribution as a function of r is already given by Equation 73 at time $t = 0$, then by integrating Equation 77 it follows:

$$r^\star(t) = r^\star(t = 0) \cdot \sqrt{1 + \frac{t}{\tau_R'}} \,, \tag{79}$$

where τ_R' is a constant with the dimension of a time:

$$\tau_R' = \frac{3\nu\gamma_R \left[r^\star(t = 0)\right]^2 \mathscr{R} T}{4\sigma k c_0 V_m^2} \,. \tag{80}$$

Using Equation 76 and Equation 79 it follows from Equation 73:

$$f(r, t) = \frac{\varrho h_R(\varrho)}{\left(1 + \frac{t}{\tau_R'}\right)^2} \cdot \text{const.} \tag{81}$$

Inserting Equation 81 into Equation 35 gives, taking into account Equation 52, Equation 79 and Equation 80 the differential equation:

$$\left(\frac{2\varrho^2}{\gamma_R} - 6\varrho + 6\right) \cdot \frac{dh_R(\varrho)}{d\varrho} + \left(\frac{10\varrho}{\gamma_R} - 6\right) \cdot h_R(\varrho) = 0 \,. \tag{82}$$

Since the time t no longer appears explicitly in Equation 82, the approach in Equation 73 is justified for quasi-stationary conditions. To calculate the function $h_R(\varrho)$ from the differential Equation 82, the parameter γ_R that occurs in it must first be determined, which is given by Equation 75. If Equation 82 is multiplied by ϱ^2 and integrated by parts between $\varrho = 0$ and ϱ, it follows:

$$\left(\frac{2\varrho^2}{\gamma_R} - 6\varrho + 6\right) \cdot \varrho^3 h_R(\varrho) - 18 \cdot \left[\int_0^\varrho h_R(\varrho) \cdot \varrho^2 \, d\varrho - \int_0^\varrho h_R(\varrho) \cdot \varrho^3 \, d\varrho\right] = 0 \,. \tag{83}$$

In Equation 83 the difference of the integrals for $\varrho \to \infty$ vanishes with respect to Equation 75. This results in the following condition for determining the parameter γ_R:

$$\lim_{\varrho = \infty} \left[\left(\frac{2\varrho^2}{\gamma_R} - 6\varrho + 6\right) \cdot \varrho^3 h_R(\varrho)\right] = 0 \,. \tag{84}$$

The expression

$$\frac{2\varrho^2}{\gamma_R} - 6\varrho + 6$$

appearing in Equation 82 to Equation 84 has a minimum for $\varrho = \frac{3\gamma_{\mathrm{R}}}{2}$ with one associated function value $6 - \frac{9\gamma_{\mathrm{R}}}{2}$. If one heuristically sets the latter expression equal to zero, one gets $\gamma_{\mathrm{R}} = \frac{4}{3}$ and hereby from Equation 82:

$$\frac{\mathrm{d}\ln(h_{\mathrm{R}})}{\mathrm{d}\varrho} = -\frac{\frac{15}{2}\varrho - 6}{\frac{3}{2}\varrho^2 - 6\varrho + 6} = \frac{5}{2 - \varrho} - \frac{6}{(2 - \varrho)^2} \, . \tag{85}$$

Integration and taking into account Equation 74 gives:

$$h_{\mathrm{R}}(\varrho \leqq 2) = \left(\frac{2}{2 - \varrho}\right)^5 \cdot e^{-\frac{3\varrho}{2 - \varrho}} \, , \tag{86a}$$

$$h_{\mathrm{R}}(\varrho \geqq 2) = 0 \, . \tag{86b}$$

With Equation 86a and Equation 86b we have Equation 84 for both $\varrho = \infty$ and for the practical upper limit $\varrho = 2$ satisfied. If, on the other hand, one assumes $\gamma_{\mathrm{R}} < \frac{4}{3}$ or $\gamma_{\mathrm{R}} > \frac{4}{3}$, then Equation 84 cannot be fulfilled. For $\gamma_{\mathrm{R}} > \frac{4}{3}$ the function $h_{\mathrm{R}}(\varrho)$ calculated from Equation 82 becomes for large values of ϱ inversely proportional to ϱ^5 and the left side of Equation 84 tends to a finite limit. For $\gamma_{\mathrm{R}} < \frac{4}{3}$, $h_{\mathrm{R}}(\varrho)$ approaches infinity for a finite value of ϱ and Equation 84 cannot be fulfilled either. Therefore, only $\gamma_{\mathrm{R}} = \frac{4}{3}$ comes into consideration.

Under the conditions considered here, one gets for the mean radius $\bar{r}$ by using Equation 73 and Equation 86a and introducing

$$u = \frac{6}{2 - \varrho}$$

as the integration variable:

$$\bar{r} = \frac{\int_0^\infty f(r) \cdot r \, \mathrm{d}r}{\int_0^\infty f(r) \, \mathrm{d}r} = r^\star \cdot \frac{\int_0^2 h_{\mathrm{R}}(\varrho) \cdot \varrho^2 \, \mathrm{d}\varrho}{\int_0^2 h_{\mathrm{R}}(\varrho) \cdot \varrho \, \mathrm{d}\varrho} = \frac{8}{9} \cdot r^\star \, . \tag{87}$$

With $\gamma_{\mathrm{R}} = \frac{4}{3}$ one obtains from Equation 80 and Equation 87:

$$\tau_{\mathrm{R}}' = \frac{\nu \left[r^\star(t = 0)\right]^2 \mathscr{R} T}{\sigma k c_0 V_m^2} = \left(\frac{9}{8}\right)^2 \cdot \frac{\nu \left[\bar{r}(t = 0)\right]^2 \mathscr{R} T}{\sigma k c_0 V_m^2} \, . \tag{88}$$

Insertion of Equation 86a into Equation 81 yields:

$$f(r,t) = \frac{\text{const.}}{\left(1 + \frac{t}{\tau_R'}\right)^2} \cdot \varrho \cdot \left(\frac{2}{2 - \varrho}\right)^5 \cdot e^{-\frac{3\varrho}{2 - \varrho}}$$

$$\text{for} \quad \varrho = \frac{r}{r^\star} \leqq 2\,, \tag{89a}$$

$$f(r,t) = 0 \text{ for} \quad \varrho = \frac{r}{r^\star} \geqq 2\,. \tag{89b}$$

From Equation 89a one obtains for the value of ϱ at which f or $\ln(f)$ has a maximum as a function of ϱ the equation $4\varrho^2 - 4 = 0$ with the solution $\varrho = 1$.
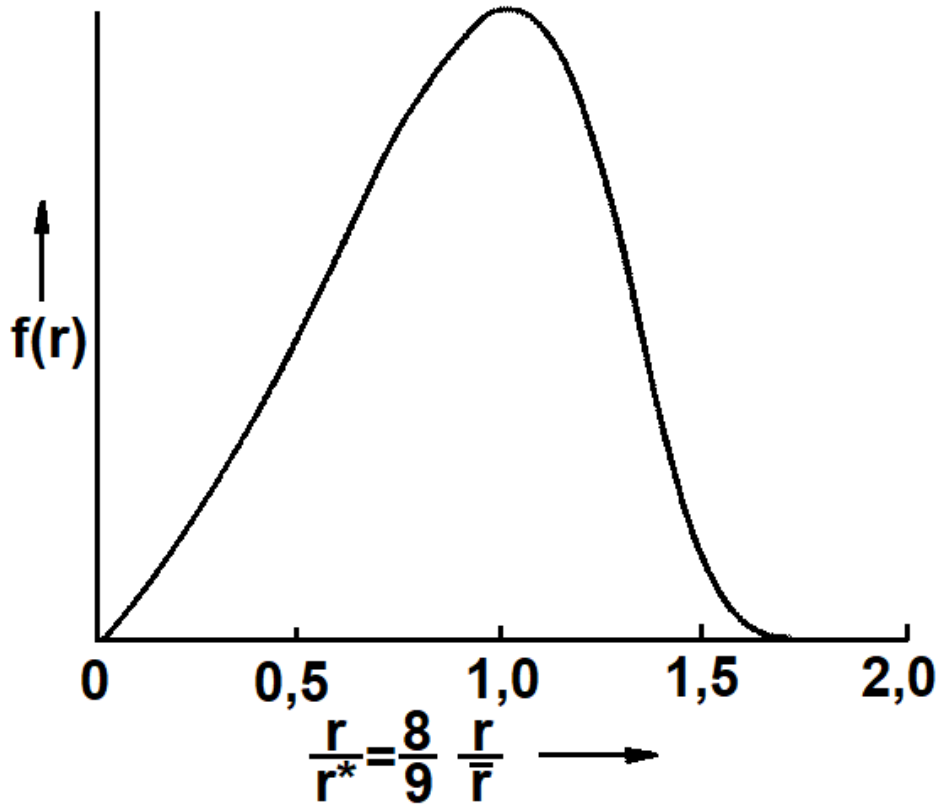

Figure 3: Quasi-stationary distribution curve for reaction-controlled mass transfer

Figure 3 shows the course of the distribution function obtained in this way for reaction-controlled mass transfer.

For $t \gg \tau_{\mathrm{R}}'$ the approximate equation is obtained from Equation 79, Equation 87 and Equation 88:

$$\boxed{\bar{r}(t) \cong \bar{r}(t=0) \cdot \sqrt{\frac{t}{\tau_{\mathrm{R}}'}} = \frac{8}{9} \cdot \sqrt{\frac{\sigma k c_0 V_m^2 \cdot t}{\nu \, \mathscr{R} \, T}}}, \tag{90}$$

if $k\bar{r} \ll \mathscr{D}$ and $t \gg \tau_{\mathrm{R}}'$ or $\bar{r}(t) \gg \bar{r}(t=0)$.
Furthermore, for Z one obtains from Equation 15 by substituting Equation 73 and Equation 76 using Equation 52:

$$\boxed{Z = \frac{3\varphi}{4\pi \cdot [r^\star(t)]^3} \cdot \frac{\int_0^2 h_{\mathrm{R}}(\varrho) \cdot \varrho \, \mathrm{d}\varrho}{\int_0^2 h_{\mathrm{R}}(\varrho) \cdot \varrho^4 \, \mathrm{d}\varrho}}. \tag{91}$$

According to Equation 78, the integral in the numerator is $\gamma_{\mathrm{R}} = \frac{4}{3}$. For the integral in the denominator, using

$$u = \frac{6}{2 - \varrho}$$

as the integration variable, one obtains:

$$\int_0^2 h_{\mathrm{R}}(\varrho) \cdot \varrho^4 \, \mathrm{d}\varrho = -\frac{64}{9} + 2^5 e^3 \cdot \int_3^\infty e^{-u} \frac{\mathrm{d}u}{u} = 1,27 \,. \tag{92}$$

Inserting Equation 79, Equation 87 and Equation 92 into Equation 91 results for longer observation times in:

$$\boxed{Z \cong \frac{\varphi}{1,27 \cdot \pi} \cdot \sqrt{\left(\frac{\nu \, \mathscr{R} \, T}{\sigma k c_0 V_m^2 \cdot t}\right)^3}}, \tag{93}$$

if $k\bar{r} \gg \mathscr{D}$ and $t \gg \tau_{\mathrm{R}}'$ or $\bar{r}(t) \gg \bar{r}(t=0)$.
As a special case of a reaction-controlled mass transfer, TODES and KHRUSCH-CHEW have calculated the redistillation of mercury between droplets of different sizes assuming the HERTZ-KNUDSEN evaporation equation and have compared their measurements with those of LIALIKOV, [7]. In the work of TODES and KHRUSHCHEV there are analogous relationships to Equation 69, Equation 70 and Equation 93, however, without the quasi-stationary distribution function having been calculated according to Equation 89a and Equation 89b

9 Discussion

In connection with experimental questions, the Equation 47, Equation 69 and Equation 70 for diffusion-controlled mass transfer as well as the Equation 49, Equation 90, Equation 91 and Equation 93 for reaction-controlled mass transfer are particularly important. The interfacial free enthalpy σ appears in these equations, the value of which is not readily available for crystals. The free enthalpy of the interface of ionic crystals with respect to the vacuum or saturated vapor is available from lattice theoretical calculations, [1]. Especially for ionic crystals with monovalent cations and monovalent anions, values of the order of magnitude $100\,\mathrm{erg\,cm^{-2}}$ are obtained. Significantly larger values are obtained for ionic crystals with higher-valued ions. However, the free enthalpy of the interface between an ionic crystal and an adjacent saturated aqueous solution, which is relevant in the present context, is significantly lower due to the reduction in the electrostatically induced parts of the energy because of the high dielectric constant of water. According to considerations by KAHLWEIT, [5], one can assume that the relevant value of σ is between $20\,\mathrm{erg\,cm^{-2}}$ to $40\,\mathrm{erg\,cm^{-2}}$ at room temperature, i.e. approximately the same order of magnitude as the interfacial tension between organic liquids and aqueous solutions. It should be expressly pointed out that the value of σ for the interface between an ionic crystal and an aqueous solution depends on the composition of the latter and can be reduced in particular by surface-active additives. An excess of one of the two types of ions contained in the crystal can have the same effect.

In Equation 47 and Equation 69 for diffusion-controlled mass transfer, only the 3rd root of σ occurs. An estimated value σ is therefore sufficient to indicate with the help of Equation 47 whether a size distribution is practically stable, or to calculate with the help of Equation 69 the average particle radius r after a given aging time. Here Equation 47 and Equation 69 can be used complementary, i.e. depending on the initial value $\bar{r}(t=0)$ the preconditions to use one or the other equation are in general fullfilled. From Equation 69 it follows, in accordance with known empirical facts, that the higher the solubility c_0, the larger the mean particle radius achieved after a given aging time.

In order to facilitate the application of the above considerations, the mean radii $\bar{r}(t)$ expected according to Equation 69 for different solubilities c_0 and observation times t are shown in Figure 4 using the following representative values: $\nu = 1$, $\sigma = 30\,\mathrm{erg\,cm^{-2}}$, $V_m = 30\,\mathrm{cm^3\,mol^{-1}}$, $\mathscr{D} = 1 \times 10^{-5}\,\mathrm{cm^2\,s^{-1}}$, $T = 298\,^\circ\mathrm{K}$ (corresponding to $25\,^\circ\mathrm{C}$).

Diffusion-controlled mass transfer is only a possible limiting case. Existing observations indicate that in many systems the rate of mass transfer is reaction-controlled. First of all, it generally follows from Equation 30 that the time change $\dot{r}$ of the radius of a particle has the greatest value when $kr \gg \mathscr{D}$, i.e. when there is nearly an equilibrium at the phase boundary. Accordingly, the temporal changes of $\bar{r}$ and Z also have maximum values when $k\bar{r} \gg \mathscr{D}$.
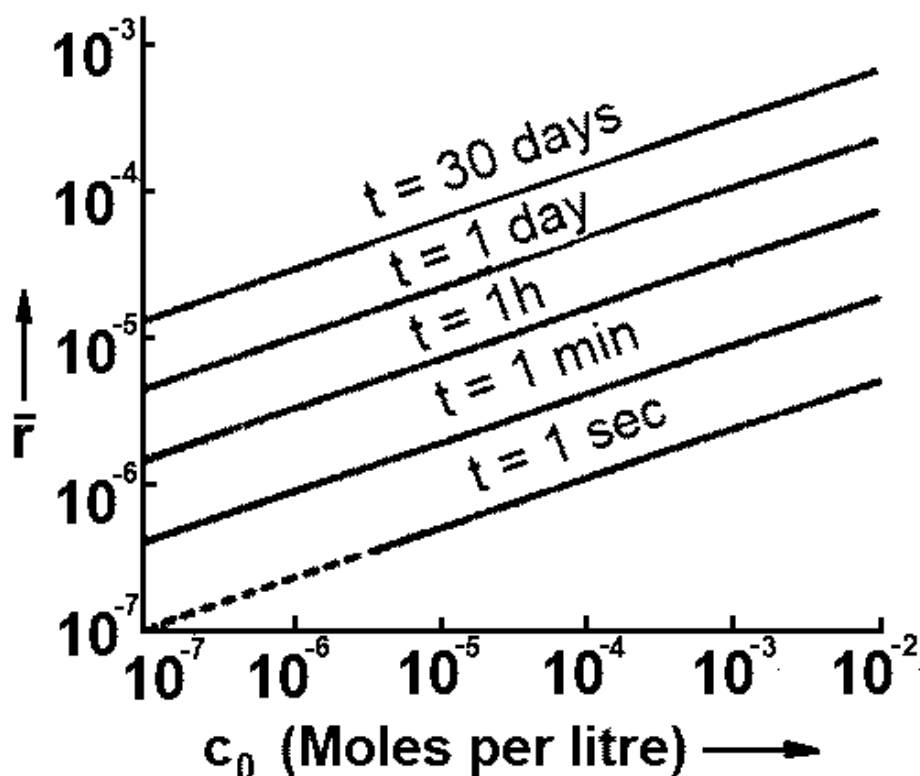
Figure 4: Mean particle radius $\bar{r}$ after a given time t as a function of solubility c_0 for diffusion-controlled mass transfer according to Equation 69 for $r(t) \gg \bar{r}(t = 0)$

Now, in general, the value of k is not available. Without knowledge of the ratio $\frac{k\bar{r}}{\mathscr{D}}$, Equation 69 or Figure 4 only gives an upper limit of the achievable mean particle radius within a given observation time t . Accordingly, Equation 70 gives a lower limit for the particle number Z.

If in a system the experimental value of $r(t)$ is significantly smaller than the value for diffusion-controlled mass transfer calculated from Equation 69, then one can conclude that the mass transfer is essentially reaction-controlled.

As an additional criterion for distinguishing between diffusion- and reaction-controlled mass transfer, one can use the shape of the distribution curve $f(r, t)$ for small values, since with diffusion-controlled mass transfer f is proportional to r^2, but with reaction-controlled mass transfer it is increasing directly proportional to r. This criterion is independent of an estimate for σ, but requires a sufficiently precise experimental determination of the distribution function, especially for small values of r, which is by no means easy.

However, Equation 49 and Equation 90 cannot easily be used for predictions, since the relevant quantity appears to be the rate constant k of the mass transfer between

the dispersed phase and the surrounding solution. In this case one can calculate k from observed values $\bar{r}(t)$ using Equation 90:

$$k \cong \frac{81}{64} \cdot \frac{[\bar{r}(t)]^2 \mathscr{R} T}{\sigma c_0 V_m^2 t} \,, \quad \text{if } \bar{r}(t) \gg \bar{r}(t=0) \,. \tag{94}$$

Experimentally, Z is easier and more precise to determine than $\bar{r}$. Therefore, it is more convenient to calculate k using Equation 93:

$$k = \frac{\nu \mathscr{R} T}{\sigma c_0 V_m^2 t} \cdot \sqrt[3]{\left(\frac{\varphi}{1,27 \cdot \pi Z} \right)^2} \,, \quad \text{if } Z(t) \ll Z(t=0) \,. \tag{95}$$

The use of Equation 95 is particularly suitable for relatively poorly soluble substances where determining the rate of growth or dissolution using the usual macroscopic methods is difficult. Investigations into the reduction of k by specifically adsorbed components in the solution (higher-value foreign ions, organic dyes) are likely to be of particular interest, even if statements using Equation 95 are not immediately clear, since on the right hand side of Equation 95 an estimated value of σ should be used, which is also influenced by solution additives, but probably generally to a lesser extent than k.

It is outside the scope of this work to discuss the test results on individual systems. However, one fact should be pointed out. It is known that a precipitate of AgCl ages much more quickly than a precipitate of $BaSO_4$. The solubilities and diffusion coefficients for both substances are approximately the same. According to the double charge of the ions in $BaSO_4$, a slightly larger value of σ is to be expected for this substance than for AgCl. If the mass transfer for both systems were controlled by diffusion, the mean particle radius $\bar{r}$ that can be achieved after a given time t should be at least as large for $BaSO_4$ as for AgCl. The opposite finding is explained by the fact that the mass transfer for $BaSO_4$ is reaction-controlled, as was shown by KAHLWEIT, [4], by tracking the temporal change in the electrical conductivity of supersaturated $BaSO_4$ solutions with particle sizes in the range of $0.1\,\mu m$ to $1\,\mu m$, while under similar conditions a diffusion-controlled mass transfer was found for AgCl.

In the above considerations it is assumed that the solubility according to the GIBBS-THOMSON equation and the growth rate are unique functions of the particle size. These assumptions are not always fulfilled. A larger crystal may contain more structural defects and therefore may have a higher chemical potential than a smaller crystal. This is the only way it is possible for new nuclei to form on the base of a large crystal during the cathodic deposition of silver from silver nitrate solution, as KOHLSCHÜTTER and TORRICELLI, [6], have observed. Furthermore, it is known that the growth rate of a crystal can depend significantly on the number of dislocations, so that different values of k shall be used for different crystal individuals. It is therefore possible that deviations from the distribution function

shown in Figure 3 occur, especially in reaction-controlled mass transfer.

For crystals that are distributed in a second solid phase as a matrix, i.e. especially in alloys, another factor to be taken into account is the occurrence of local stresses that occur during the growth of the dispersed particles and which are compensated only within a certain delay through diffusion or plastic flow of the atoms of the surrounding matrix. LIFSHITZ and SLYOZOV, [9, 10], have pointed this out and announced a more detailed investigation.

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